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NOVEL REAGENTS FOR CHEMICAL VAPOR DEPOSITION OF INTERMETALLIC ALLOYS

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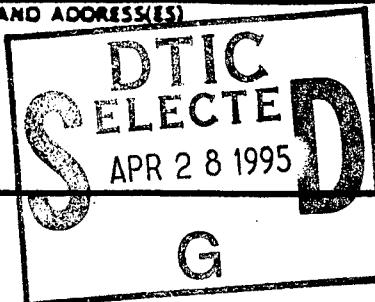
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13. ABSTRACT (Maximum 200 words)

Reactions of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ with AlMe_3 proceed by formation of covalently bonded heterobimetallic intermediates with no alkyl exchange. Reaction with $\text{AlH}_3 \cdot \text{NMe}_3$ yielded $\text{Al}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{NMe}_3$ and " $\text{Hf}(\text{CH}_2\text{SiMe}_3)_3\text{H}_3$ ". Carbon blocks coated with this mixture produced a HfAlC_2 coating which was effective in protecting the substrate from air oxidation at high temperatures.

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FINAL PROJECT REPORT

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PUBLICATIONS:

"Alkyl for Hydride Exchange Between Alane-Trimethylamine and Group IVB Metal Alkyls

William G. Feighery, Rein U. Kirss, Charles H. Lake, and Melvyn Rowen Churchill, *Inorg. Chim. Acta*, 1994, 218, 47-51.

"Reactions of Tetrakis(trimethylsilylmethyl)hafnium With Trimethylaluminum

Rein U. Kirss, William G. Feighery, and Douglas C. Gordon, *Inorg. Chim. Acta*, 1994, in press

ABSTRACT:

Alkyl exchange reactions between group IVB transition metal alkyls (MR_4 where $M = Ti, Zr, Hf$ and $R = Me_3CCH_2, Me_3SiCH_2$) and aluminum alkyls (AlR_3 , where $R = Me, Et, H$) were studied by multinuclear NMR spectroscopy ($^1H, ^{13}C, ^{27}Al$). In the case of $Hf(CH_2SiMe_3)_4$ and $AlMe_3$, evidence for the formation of neutral bimetallic complexes was observed without the observation of alkyl exchange. Reactions between $Hf(CH_2SiMe_3)_4$ and $AlH_3 \cdot NMe_3$ yielded $Al(CH_2SiMe_3)_3 \cdot NMe_3$ and " $HfH(CH_2SiMe_3)_3$ ". The former was characterized by single crystal x-ray diffraction. In all other exchange reactions, decomposition was too rapid for the observation of alkyl exchange or intermediates. Pyrolysis of $Hf(CH_2SiMe_3)_4 / AlH_3 \cdot NMe_3$ mixtures yielded black powders which analyzed for " $HfAlC_2$ ". Carbon blocks were dip-coated with $Hf(CH_2SiMe_3)_4 / AlH_3 \cdot NMe_3$ mixtures and pyrolyzed to give an mixed metal oxide / metal carbide coatings which gave some measure of oxidation protection at $600^\circ C$.

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Introduction

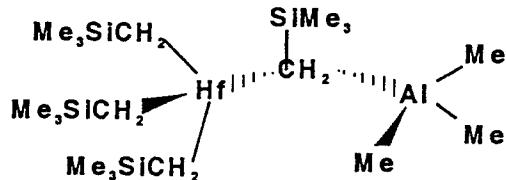
We have been investigating molecular precursors for the chemical vapor deposition of intermetallic alloys of aluminum and group IVB transition elements (Ti, Zr, and Hf) on carbon substrates as oxidation protection for the carbon materials. Our efforts have been concentrated in three areas:

1. investigations of the alkyl exchange reactions between group IVB and aluminum alkyls,
2. preparation and characterization of ternary aluminum/group IVB metal carbides from molecular precursors, and
3. evaluation of coatings prepared from molecular precursors in 2 with respect to oxidation protection of carbon blocks.

Further details of each of these projects is provided in the attached manuscripts/reprints.

Exchange Reactions

Reactions between $TiMe_4$, Cp_2ZrMe_2 or $Hf(CH_2SiMe_3)_4$ and $AlMe_3$ were investigated using conductivity measurements and 1H NMR spectroscopy. Little change was observed in the conductivity of $Hf(CH_2SiMe_3)_4/AlMe_3$ or $AlMe_3/Cp_2ZrMe_2$ mixtures in dichloromethane relative to the molar conductivity of the reactants. In the presence of PEt_3 , a small increase in conductivity was observed for the latter solution. A fifty fold increase in the conductivity was observed in mixtures of $TiMe_4$ and $AlMe_3$. Spectroscopic studies on mixtures of $Hf(CH_2SiMe_3)_4$ and $AlMe_3$ were consistent with formation of a thermally unstable, alkyl bridged heterobimetallic complex, 1, present in a 5:1 ratio to the starting materials. There was no evidence for alkyl exchange in these reactions.



1

Reaction of equimolar amounts of $AlH_3.NMe_3$ and $M(CH_2SiMe_3)_4$ in benzene (for $M=Zr, Hf$) led to exchange of all three Al-H bonds for Al-CH₂SiMe₃ bonds and isolation of $Al(CH_2SiMe_3)_3.NMe_3$ (2).

The latter compound crystallized in the P1 space group, a 9.535(2), b 10.913(2), c 12.273(2) Å, α 88.03(1), β 86.03(1), γ 86.93(1)°, U 1271.6(4) Å³, D_c 1.002 g cm⁻³, Z =2, μ (Mo-Kα) 0.217 mm⁻¹, $F(000)$ =424. Similar reactions between AlH₃·NMe₃ and Cp₂ZrR₂ (R = CH₃, CH₂SiMe₃) yielded Cp₂ZrH₂ and AlR₃·NMe₃. Reaction of AlH₃·NMe₃ with Zr(CH₂Ph)₄ produced Al(CH₂Ph)₃·NMe₃.

Preparation of Ternary Group IVB Aluminum Carbides From Molecular Precursors

Reaction of Hf(CH₂SiMe₃)₄ or Zr(CH₂SiMe₃)₄ with one equivalent of AlH₃·NMe₃ in solution, followed by evaporation of the solvent and pyrolysis of the residue under argon (850°C for 16 hours), yielded a black crystalline powder, impervious to all mineral acids and strong oxidizing solutions.

Combustion analyses for C, H and N were consistent with a formulation as HfAlC₂ and ZrAlC_{1.4}. EDX analysis revealed the presence of both aluminum and hafnium in the HfAlC₂ product. Silicon was not detected in the latter measurements. The reaction of Ti(CH₂SiMe₃)₄ with AlH₃·NMe₃ at room temperature resulted in immediate decomposition without detection of any intermediates. Combustion analysis of the annealed products from reactions of Ti(CH₂SiMe₃)₄/AlH₃·NMe₃ were consistent with the formulations TiAlC_{1.2} based on retention of the initial 1:1 stoichiometry of the metals.

Evaluation of HfAlC₂ Coated Carbon Blocks In An Oxidative Environment

When solutions generated from Hf(CH₂SiMe₃)₄ and AlH₃·NMe₃ were used to coat carbon blocks and annealed under argon, thin coatings of the HfAlC₂ phase were obtained. ESCA analysis (Table 1) of the coated blocks were consistent with a 1:1:2 stoichiometry for the three elements, respectively, however, large amounts of oxygen, most likely in the form of metal oxides was also observed. The most likely source of metal oxides is believed to be the result of atmospheric oxygen introduced during the annealing process through small leaks in the system combined with high annealing temperatures and long annealing times. This conclusion is supported by the nearly constant or slightly increasing concentrations of aluminum and hafnium as a function of depth while the oxygen concentration decreases steadily when sputtered below the surface layer. The formation of metal oxides is not necessarily a major problem for coatings applications, as air oxidation of the metal carbide coating to metal

oxides is anticipated to be the mechanism for protection of the substrate. Alumina in particular has been investigated as oxidation resistant coatings for carbon based materials. Powder diffraction experiments on the coated blocks reveal a single major peak likely to correspond to diffraction by the carbon substrate. Smaller, broader peaks were too weak in intensity to identify the nature of the coating (Figure 1).

Table 1: ESCA Analysis Of T300 Carbon Blocks Coated From $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$

| Coating Solution | Depth (Å) | $\text{AlH}_3\cdot\text{NMe}_3$ Mixtures | | Atom % | | |
|-----------------------------------|--------------|------------------------------------------|------|--------|------|------|
| | | Hf | Al | Si | C | O |
| single coat from hexane solution | surface | 11.3 | 25.0 | 5.2 | 31.2 | 27.3 |
| | 20 | 11.9 | 26.3 | 4.7 | 28.1 | 29.0 |
| | 3000 | 8.8 | 5.8 | 0 | 72.4 | 13.0 |
| triple coat from benzene solution | surface | 4.4 | 9.2 | 6.4 | 42.5 | 37.5 |
| | 20 | 5.8 | 9.1 | 5.7 | 39.4 | 40.0 |
| | 320 | 6.9 | 6.2 | 3.4 | 58.7 | 24.8 |

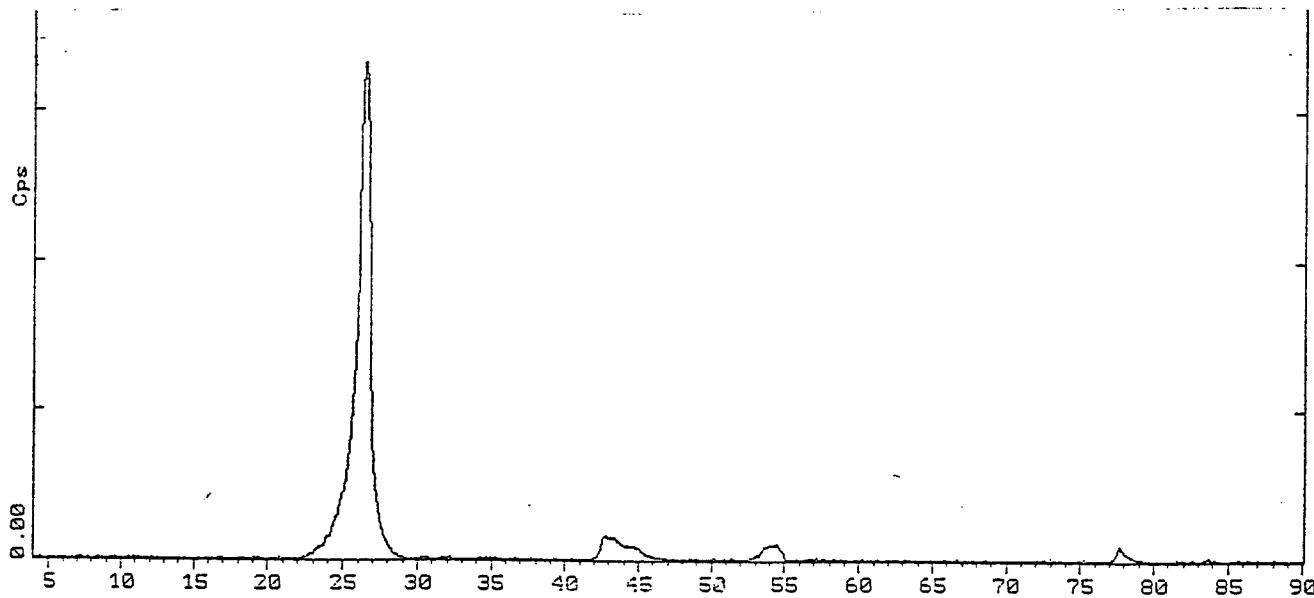


Figure 1: X-ray Powder Diffraction Pattern of T300 Block Coated With "HfAlC₂"

The oxidation behavior of carbon blocks coated with a single layer of mixed metal carbides from $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4 / \text{AlH}_3\cdot\text{NMe}_3$ mixtures coated blocks was evaluated by pyrolysis in air at 600°C and 900°C with the results summarized in Table 2. The data show that the HfAlC₂ coating acts to protect the underlying carbon substrate for short periods, although the degree of protection from this single coating is understandably far from optimal. The 41% ceramic yield of HfAlC₂ from mixtures of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{AlH}_3\cdot\text{NMe}_3$ was expected to produce cracks and pinholes in the coating exposing the underlying carbon

substrate to air oxidation. The concentration of the coating solution has a measurable effect on the oxidation behavior of the blocks. The highest concentrations appear to leave thicker coatings more susceptible to cracking as observed by SEM. Very dilute solutions provide for inadequate surface coverage, exposing the substrate to rapid air oxidation. Coatings prepared from benzene solutions of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and AlH_3NMe_3 were observed to be superior than coatings prepared in hexane solution.

Table 2: Oxidation Protection of T300 Carbon Blocks By A Single Coat of HfAlC_2

| <u>Concentration of Coating Solution</u> | % Weight Loss after 4 hours at 600°C | % Weight Loss after 4 hours at 900°C |
|------------------------------------------|--------------------------------------|--------------------------------------|
| Uncoated T300 | 28.5 | 85.5 |
| 1.0 M | 21.4 | 61.6 |
| 0.1 M | 16.6 | 32.6 |
| 0.05 M | 11.5 | 35.6 |
| 0.01 M | 13.3 | 85.3 |

The effect of multiple coatings on the oxidation behavior of carbon blocks are summarized in Table 3. The multiple coated blocks were prepared at a constant concentration of 0.1 M for the coating solution by repetition of the coating and annealing cycles as described above for the single coated blocks.

Table 3: Oxidation Protection of T300 Carbon Blocks By Multiple Coats Of HfAlC_2

| <u>Number of Coating Annealing Cycles</u> | % Weight Loss 600°C/4 h | % Weight Loss 600°C/10 h | 900°C |
|-------------------------------------------|-------------------------|--------------------------|-------|
| 1 | 12.0 | 40.2 | |
| 2 | 15.9 | 40.7 | 35.6 |
| 3 | 16.92 | 29.0 | |

As expected, the rate of oxidation increases with temperature. The rate of oxidation (Figures 2-4) for the different number of coatings appears to be qualitatively the same for the single, double and triple coated blocks, suggesting that 1) multiple coatings are unable to fill the space left by the initial coating (i. e. pinholes, cracks are of molecular dimensions) or 2) the coating materials themselves are chemically modified and either consumed or detached from the block exposing the carbon substrate to air oxidation. Prolonged oxidation of a triple coated block at 900°C (8 hours) leads to complete consumption of the carbon block leaving a residual white crystalline powder identified by x-ray diffraction as HfO_2 (Figure 5).

Data from "344-18-1"

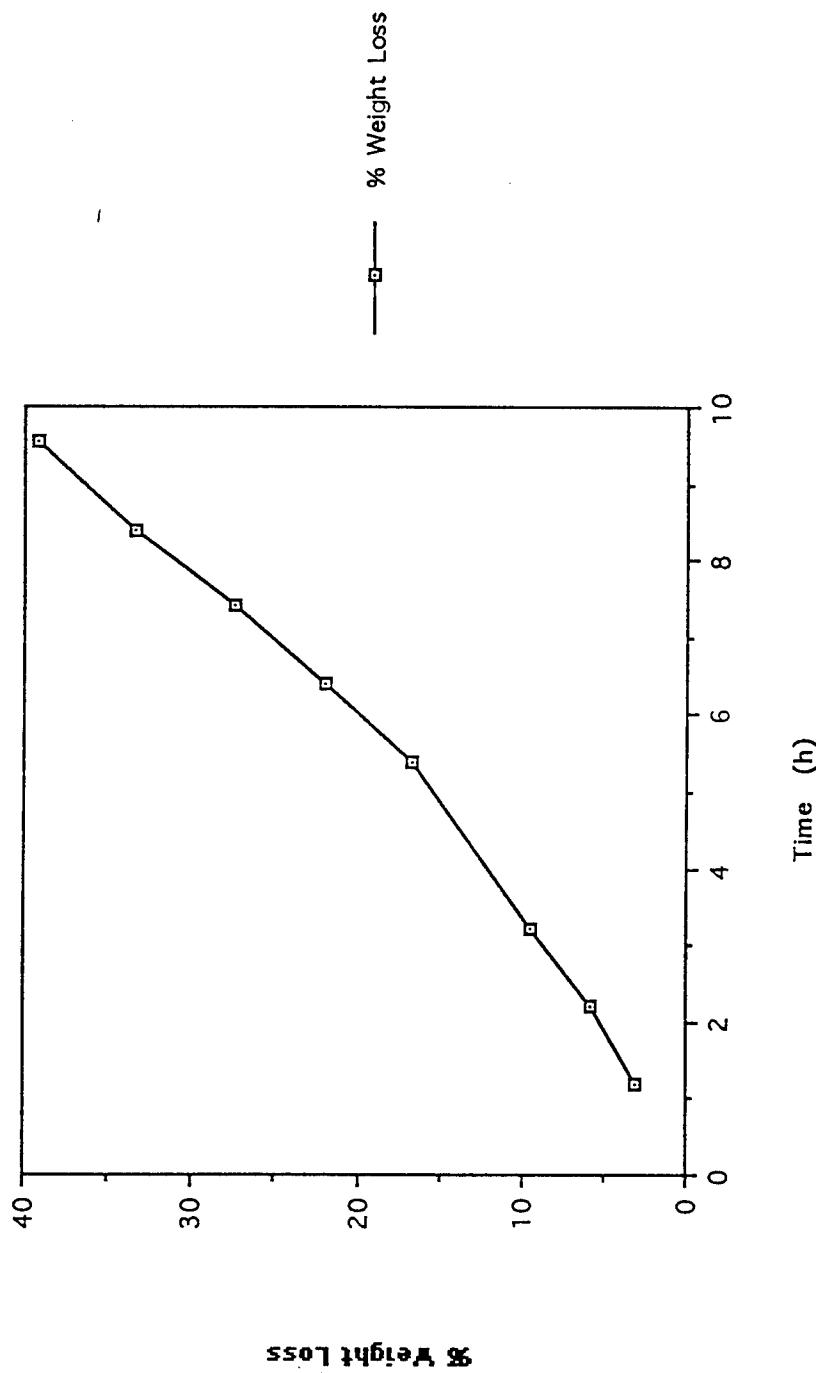


Figure 2: Oxidation Rates of Single Coated T300 Block

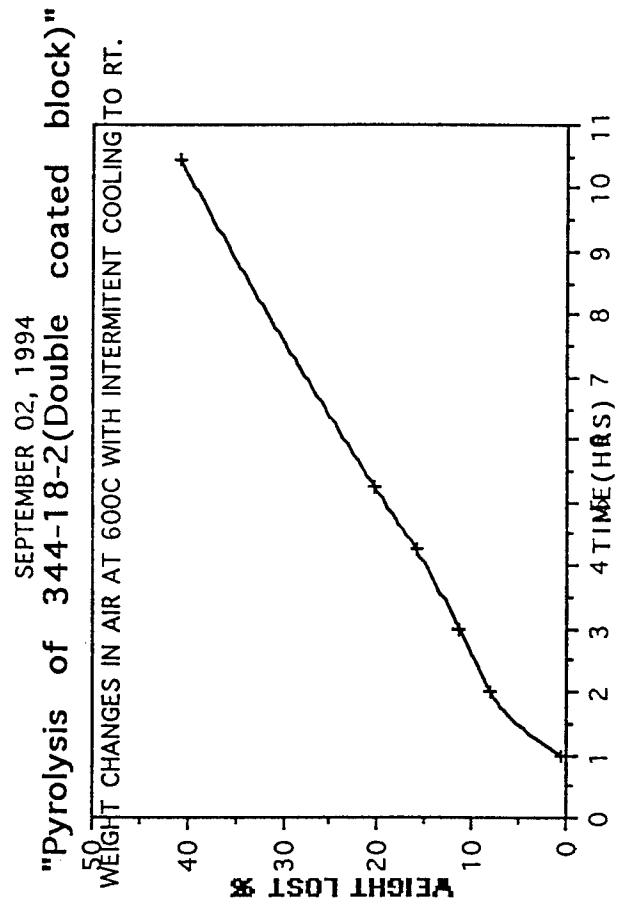


Figure 3: Oxidation Rates of Double Coated T300 Blocks

Data from "344-18-3"

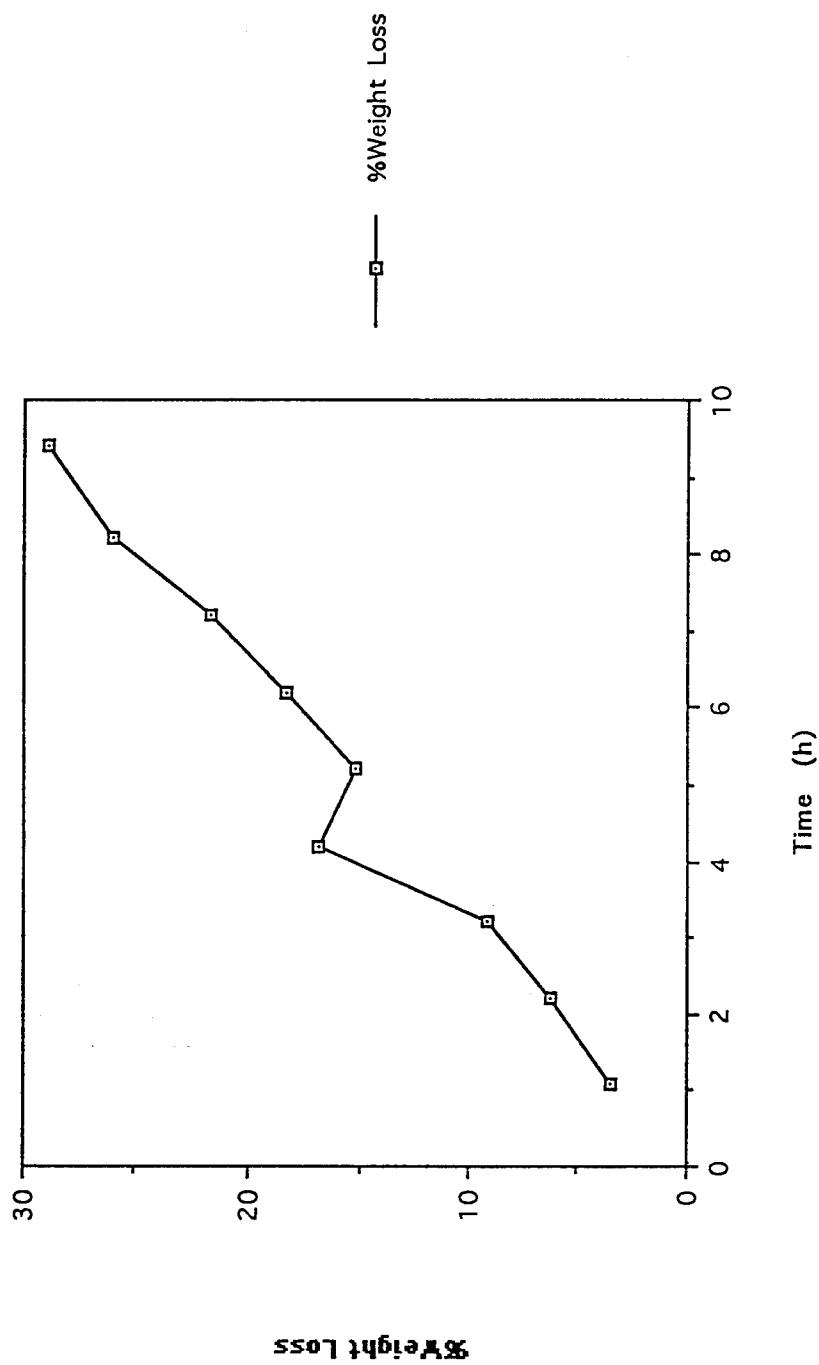


Figure 4: Oxidation Rates of Triple Coated T300 Blocks

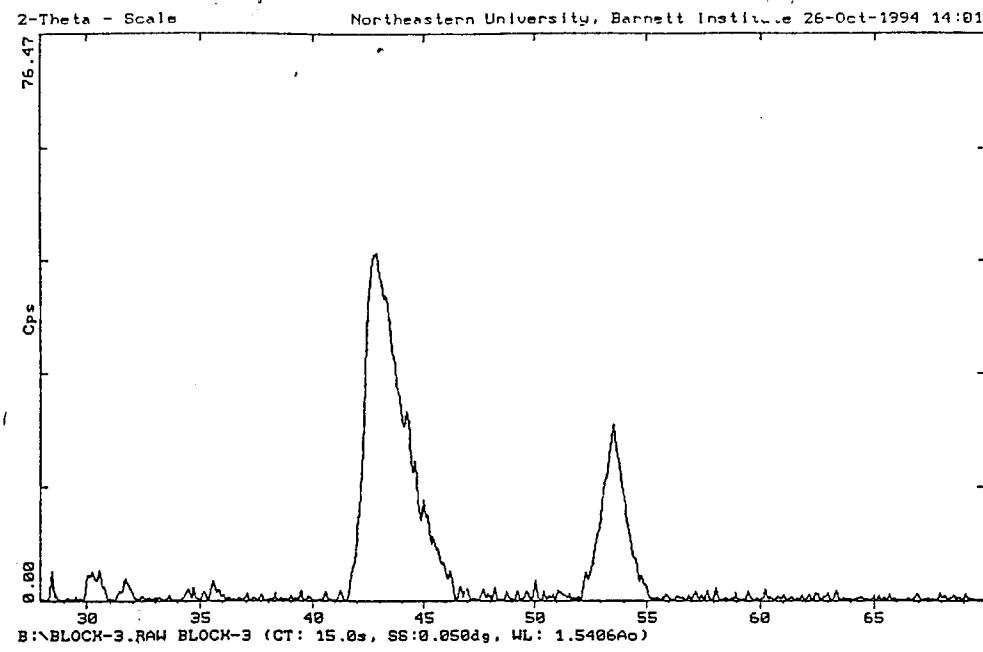


Figure 5: X-ray Powder Diffraction Pattern of Residue From Complete Pyrolysis Of A T300 Block Coated With "HfAlC₂"

The fate of the aluminum present initially in the coating remains undetermined, although it is possible that the diffraction pattern in Figure 5 contains a mixture of Al₄C₃, Al₂O₃ and HfO₂ (Table 4).

Table 4: X-ray Powder Diffraction Data For Completely Oxidized T300 Blocks Coated With "HfAlC₂"

| 2-THETA | INTENSITY | R-INTENSITY | |
|---------|-----------|-------------|---------------------------------------------------|
| 28.439 | 4 | 8.69565217 | HfO ₂ |
| 30.194 | 5 | 10.8695652 | |
| 30.632 | 4 | 8.69565217 | |
| 31.656 | 3 | 6.52173913 | HfO ₂ , Al ₄ C ₃ |
| 34.435 | 1 | 2.17391304 | " |
| 34.654 | 1 | 2.17391304 | " |
| 35.532 | 3 | 6.52173913 | " |
| 42.844 | 46 | 100 | C |
| 43.283 | 41 | 89.1304348 | C, Al ₂ O ₃ |
| 44.234 | 24 | 52.173913 | C |
| 44.399 | 17 | 36.9565217 | |
| 44.965 | 12 | 26.0869565 | HfO ₂ |
| 50.083 | 3 | 6.52173913 | HfO ₂ |
| 53.52 | 23 | 50 | Al ₂ O ₃ |

Conclusions

The present study on the development of novel organometallic reagents for chemical vapor deposition of early transition metal and aluminum containing materials for oxidation protection of carbon substrates leads to the following conclusions:

1. Alkyl exchange between volatile alkyl group IVB transition metals and aluminum alkyls does not occur
2. Alkyl for hydride exchange between volatile alkyl group IVB transition metals and $\text{AlH}_3\cdot\text{NMe}_3$ is rapid
3. Pyrolysis of mixtures $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{AlH}_3\cdot\text{NMe}_3$ yields ternary metal carbide products analyzing for " HfAlC_2 "
4. The material obtained from solution coating $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{AlH}_3\cdot\text{NMe}_3$ mixtures onto carbon blocks followed by annealing under argon provides a measure of oxidation protection for the underlying substrate for short time periods at temperatures in the vicinity of 600°C.